PHYSICAL REVIEW VOLUME 83, NUMBER 5 SEPTEMBER 1, 1951

The Thermal Stability of *F*-Centers in Alkali Halides*

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(Received May 7, 1951)

The R'-band reported previously in additively colored KCl has been found to contain a distinct band which, above a certain total color-center concentration, is in heterogeneous thermal equilibrium with the F-centers. The variation of the saturation concentration of F-centers with temperature has been studied and a latent heat for the dissociation of the coagulated centers has been determined.

I. INTRODUCTION

THE formation of a broad absorption band (the R'-band) on the long-wavelength side of the F-band by optical and thermal treatment of additively colored KCl has been discussed recently.[1,2] By analogy with a similar band frequently observed[3,4] in NaCl, this band might be ascribed to colloidal metal; but, except for the temperature-insensitivity of the band shape, the presence of a second phase could not be demonstrated. This was in large part the result of the simultaneous presence of absorbing centers caused by illumination in the F-band, such as R-, M-, and N-centers, in addition to any formed solely by thermal coagulation of F-centers. As a consequence, the shape and wavelength of maximum absorption of the R'-band varied considerably with the combined thermal and optical treatment.

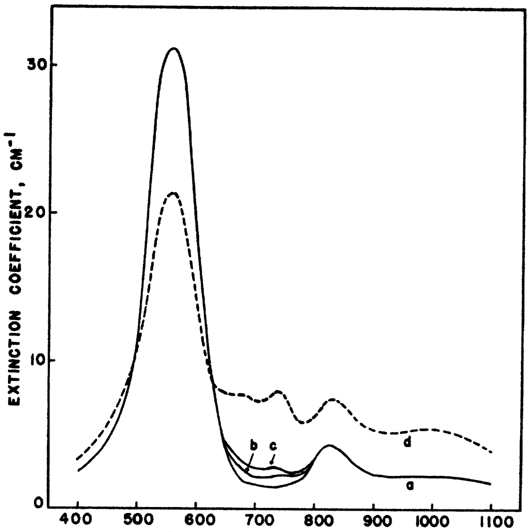

FIG. 1. Growth of R-bands during illumination.

Several preliminary experiments were undertaken to provide a basis for a systematic study of the purely thermal coagulative process. The absorption at $-195°C$ of about fifty different additively colored crystals covering a concentration range from 9×10^{16} to 1×10^{18} F-centers/cc, which were exposed to daylight and heated at several temperatures and rapidly quenched, was measured. It was observed that the prominence of the R-, M-, and N-bands bore no particular relation to the total color-center concentration or treatment temperature. The broad R'-band was both temperature and concentration dependent. On the other hand, crystals prepared and handled in complete darkness or under red light showed only the development of F- and M-bands and a quite narrow, symmetrical band in the neighborhood of 760 mμ (at room temperature) in crystals having a high concentration or after treating at the lower temperatures. Anticipating conclusions to be drawn later, we will call this band the colloidal band. Curve a, Fig. 1, and curve c, Fig. 2 illustrate the appearance of these bands at room temperature. The initial presence of the M-band is surprising, as it has previously been considered primarily as an optical product.[5,6]

The effect of brief illumination in the F-band during measurement of the spectrum is shown in Fig. 1. Curve *a* is that of a crystal prepared in the dark, the measurements made from 1100 working toward 400 mμ. Curve b was taken for the region 625–800 mμ immediately following a; curve c was obtained after 5 minutes irradiation by 560-mμ light in the spectrophotometer, and d after 2 days' exposure to daylight. It is apparent that R- and N-bands are absent prior to the measurement, and that brief exposure in the F-band causes some, but not an objectionable, growth in the R-bands and consequently a slight decrease in the F-band.

Slices of crystal containing F- and M-centers were mounted in small Al-foil holders having a horizontal slit as a spectrophotometer aperture; and, without recutting or repositioning the crystal, the absorption spectrum was measured prior to and after heat treatment to develop the colloidal band. The Smakula dispersion formula[7] was applied to the bands both before and after to obtain concentrations; and it was found

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* This work has been supported by the ONR. Presented before the one-hundred-and-nineteenth meeting of the American Chemical Society, Cleveland, Ohio, April 10, 1951. Published with the approval of the Oregon State College Monographs Committee as Research Paper No. 180, Department of Chemistry, School of Science.

[1] A. B. Scott and L. P. Bupp, Phys. Rev. **79**, 341 (1950).

[2] Scott, Hrostowski, and Bupp, Phys. Rev. **79**, 346 (1950).

[3] E. Mollwo, Nachr. Ges. Wiss. Göttingen **II**, 254 (1932).

[4] M. Savostianowa, Z. Physik **64**, 262 (1930).

[5] J. P. Molnar, Phys. Rev. **59**, 944(A) (1941).

[6] S. Petroff, Z. Physik **127**, 443 (1950).

[7] A. Smakula, Z. Physik **59**, 603 (1930).

in all cases that the apparent gain in the colloidal band was very much greater than the loss in the F- and M-bands, so that it was concluded that the dispersion formula, intended to apply to electronic oscillators, cannot be applied to other types of absorbing centers even qualitatively, as has been suggested.[1,3]

To obtain quantitative information about the thermal equilibrium between F-centers and the coagulation product, the dependence of the equilibrium F-center concentration upon total color-center concentration and upon temperature was determined by the experiments to be described.

II. EXPERIMENTAL

(A) Preparation and Thermal Treatment of Crystals

All crystals were additively colored by the method previously described.[1] The time of heating was materially reduced in the case of the more dilute crystals by keeping the end of the copper pipe containing the KCl at a temperature of about 650°C and allowing the other end to extend out of the furnace. By varying the length of tube extending out of the furnace, the temperature of the cool end, and thus the vapor pressure of K, was varied to give crystals having from 1 to 10×10^{17} color centers/cc after two hours heating. The crystal having 9×10^{16} color centers/cc was prepared by using Na instead of K and heating the entire bomb at 500°C for 23 hours. After the bombs were quenched in cold water, the crystals were removed and stored in lightproof containers.

Pieces of crystal considerably larger than needed for spectrophotometric measurements were wrapped in Al foil and brought to equilibrium at a series of temperatures in a small automatically controlled muffle furnace. Temperatures were measured by means of a Chromel-Alumel thermocouple and microvoltmeter, the couple and meter being calibrated at the normal boiling point of water and the temperature of freezing KCl. Allowing for thermal gradients in the furnace and small time drifts in the controlling mechanism, the temperatures reported are correct within 5°. Following attainment of equilibrium, the foil-wrapped crystals were plunged into cold CCl_4. Numerous experiments with several quenching methods showed this to yield the highest and most reproducible concentration of F-centers at any given temperature.

Slices taken from the interior of the crystals were used for absorption measurements in the Beckman Model D-U Spectrophotometer. For the more concentrated samples, the slices could not be more than about 0.25-mm thick to avoid optical density beyond the range of the instrument; the difficulty of preparing thin sections imposed an upper concentration limit of about 8.0×10^{17} color centers/cc for absorption determinations. These slices were cut and mounted on metal holders having horizontal apertures 1.0×2.5 mm, by red safelight. They were transferred to the instrument with a minimum of exposure of subdued light, and in no case was a development of R- or N-bands noted. Following the absorption measurement, the thickness was measured by a calibrated eyepiece micrometer; only sections showing accurately parallel faces were included in the computation of concentrations.

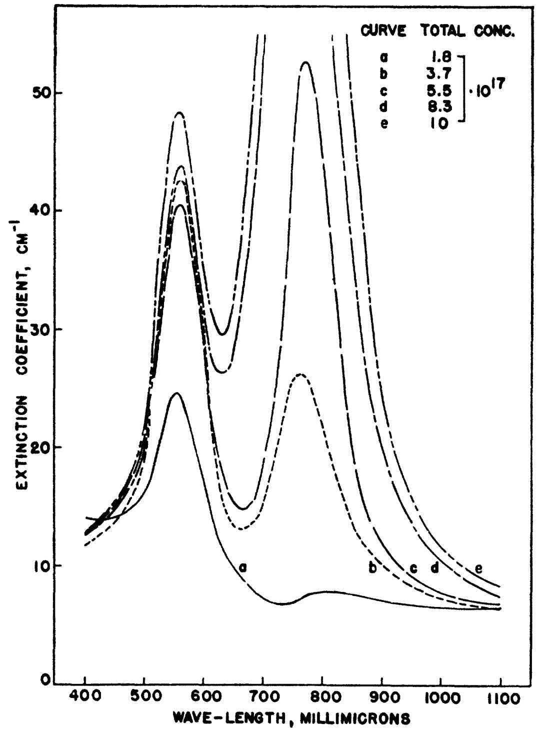

FIG. 2. Absorption curves for a series of crystals of varying concentration. Quenched from 400°C after 15 minutes.

Initially, the thermal treatments were carried out on crystals already cut to the proper thickness for absorption measurements; but a good deal of bleaching and evaporation occurred on the surface, which would tend to make measured concentrations low.

(B) Analytical Methods

For colored crystals in this concentration range, the application of the dispersion formula to absorption data is the only practicable analytical means available. An attempt was made to extend the pH-change method[1] to this concentration range, in the hope of verifying Kleinschrod's value[8] for the oscillator strength for F-centers in KCl. A small cell of about 2-ml capacity was fitted with a suitable inlet and outlet for purified nitrogen. A slightly acidified solution, boiled to expel CO_2, and having a pH in the neighborhood of 5.2, was thermostated at 25°C and the pH of the solution measured by means of a Beckmann pH meter and "micro" electrodes inserted in the cell. While nitrogen was streaming out of the cell, a crystal of KCl weighing about 200 mg was inserted and the change in pH noted

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[8] F. G. Kleinschrod, Ann. Physik **27**, 97 (1936).

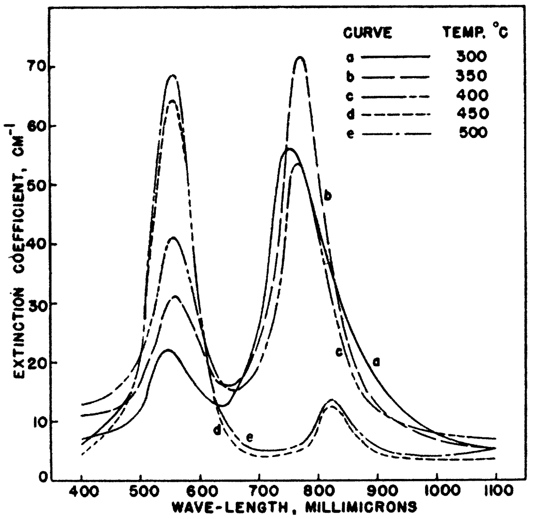

FIG. 3. Variation of F-center stability with temperature for a series of crystals of the same total concentration.

after regaining temperature. Several blank determinations were made using the single-crystal stock from which the colored crystals were prepared. The blank stock gave extremely variable pH changes which were of the order of the change computed for the colored crystals to be analyzed, so that the method could not be relied upon. Some experiments using Baker's analyzed cp KCl on a larger scale showed that it caused no significant change in pH of slightly acid CO_2-free water, so that with sufficient care in the preparation of fused single crystals, this method might prove to have sufficient sensitivity to provide an analytical method for color centers.

Kleinschrod gives no specific data on blank determinations but states that the stock material was tested and only unobjectionable pieces were used to prepare colored crystals. He did not exclude CO_2 but states the indicator used as a measure of pH was unaffected by CO_2. In general, the concentration of color centers used was considerably lower than in these experiments. While his ratios of chemically-determined to optically-determined concentration are satisfactorily constant, it is felt that his value for the oscillator strength, 0.81, cannot be considered as established without further investigation by independent means.

For this reason, the oscillator strength has been assumed to be unity, and all concentrations reported may be readily converted to the basis of any other chosen oscillator strength by dividing by the oscillator strength. The Smakula equation, using modern values for the physical constants involved then reduces to

$$n = 1.095\alpha_M W$$

for F-centers having maximum absorption at room temperature at 560 mμ in KCl, where n is the number of F-centers/cc, α_M the absorption coefficient at the maximum absorption in cm^{-1}, and W the width of the absorption curve at half-maximum in electron volts. For M-centers, having a maximum at 825 mμ, the numerical multiplier has the value 1.120; and α_M for the F-band, in the absence of an overlapping band, was taken as the difference between α at 560 mμ and the lowest value of α on the absorption curve, which generally lay in the region 1000–1100 mμ. The reference aperture used to establish 100 percent transmission was slightly narrower than those upon which crystals were mounted, so that negative optical densities were avoided and the minimum α had thus always a small, positive value. When the colloidal band is present, α_M and W of the F-band are both somewhat increased by overlapping. In the absence of more accurate means of correction for the overlap, the colloidal band was assumed symmetrical (which is not strictly true largely because of a small contribution to the absorption by M-centers) and α_M was taken as the difference between α at 560 and at 960 mμ. W should be a constant characteristic of the band at a constant temperature and was obtained by taking the average value of 30 measurements made on crystals containing F-centers, varying in concentration from 14 to 85×10^{16}/cc, and having such small concentrations of other centers that no overlapping was possible. At 25°C, W was found to be 0.359 ± 0.002 ev. This value could then be used with confidence when the F-band was broadened by overlapping of the colloidal band, and, in fact, was used in preference to individually determined W values even in the absence of the colloidal band.

Errors in absorption measurements were greatest in the case of dense crystals and, since optical densities measured were sometimes as high as 2, were of considerable magnitude. However, these errors, arising from random inaccuracies in dark-current, 100 percent transmission, and optical density settings, are random and were largely eliminated by taking the mean of sufficient concentration determinations at each temperature to reduce the probable error in the mean to less than 3 percent. However, errors in concentration arising from the foregoing choice of method for arriving at α_M and W are systematic and affect all concentrations about the same way. Estimation of this error is difficult; but an inspection of the curves showing both F- and colloidal bands will show that uncertainty in the choice of the 960-mμ absorption, rather than some other neighboring value, as the proper base for α_M calculation might introduce an error as high as 10 percent in the crystals showing greatest overlapping. In most cases the overlapping was not serious, and the probable systematic error from this source was at the outside 5 percent. The over-all probable error in the reported F-center concentrations, noting that the error in W is negligible, is thus about 7 percent. It must be emphasized that the assumption of an oscillator strength other than unity would introduce a corresponding change in all the concentrations, which are on a consistent basis among themselves.

III. DISCUSSION OF RESULTS

(A) Stability of *F*-Centers as a Function of Temperature

Figure 2 shows typical absorption curves for a series of crystals of varying total concentration held at 400°C for 15 minutes and quenched. The total concentrations were estimated from curves taken prior to the 400° treatment on neighboring sections of the crystals used, and include the concentration of *M*-centers; due to some inhomogeneity throughout large regions, these total values cannot be considered exact and actually do not enter the calculation of the equilibrium *F*-center concentration. It will be noted that α_M for the *F*-band, as defined in Sec. II, is quite constant for all crystals in which both *F*- and colloidal bands are present, regardless of total concentration. Since α_M and *F*-center concentration are proportional, this shows the equilibrium *F*-center concentration to be independent of total concentration and the equilibrium is consequently heterogeneous. A further indication is the complete absence of the 760-mμ band in the crystal having less than the saturation concentration of *F*-centers.

Curves b and c were obtained for crystals which had been previously brought to equilibrium at 300°; the fact that the saturation concentrations are the same for these two as for those in which the equilibrium was approached from the opposite direction shows that 15 minutes is a sufficient time at 400°. The time required for attainment of equilibrium was determined either in this way or by treating individual crystals for varying times and determining the time after which the *F*-concentration remained unaltered.

These times varied from 90 minutes at 300° to 45 seconds at 500°.

Figure 3 shows the variation of *F*-center stability with temperature for a series of crystals all of approximately the same total concentration. Especially to be noted is the fact that, at temperatures as low as 300°, there is a definite stable concentration of *F*-centers which is readily measurable when the total concentration is not too high and when optical bands are suppressed.

From 7 to 15 separate crystals covering a range of total concentration were studied at each of four temperatures, and the mean of the *F*-center concentrations in equilibrium with colloidal centers was obtained (Table I). Concentrations in brackets are for crystals in which the *F*-center concentration was below the mean equilibrium value and in which no colloidal band was observed. Three crystals, at or somewhat above the concentration for quantitative determination, were treated at 500° with no development of the colloidal band.

The attainment of equilibrium at 300° was tested by heating part of the samples for 90 and part for 150 minutes. It will be noted there is no significant difference in the average *F*-center concentration for the two groups. The time required at each temperature gives a rough indication of the rate of the coagulation of *F*-centers; but, until further rate studies are made, little can be said about the actual value of the activation energy.

TABLE I. Concentration of *F*-centers in equilibrium with colloid.

t, °C, and time	Approx. total concentration centers/cc $\times 10^{-16}$	*F*-centers/cc $\times 10^{-16}$	Av. equilibrium conc., *F*-centers/cc $\times 10^{-16}$
500, 45 sec	55	[56]	
	83	[>80]	
	100	[>80]	>80
450, 3 min	37	[34]	
	55	[54]	
	83	62, 73, 70 69, 69	
	100	58, 53, 54	64±2
400, 15 min	17	[17]	
	37	32, 28	
	55	29, 25	
	83	29	
	100	28, 30, 32	29±1
350, 50 min	9	[9.2]	
	23	20, 18, 17	
	34	19	
	55	22, 21	19±0.5
300, 90 min	18	9.9, 9.4, 8.3, 9.0	
	37	10.8, 11.2, 12.4	
	55	11.9, 13.6, 12.4	10.8±0.5
150 min	9	[9.2]	
	18	12.8	
	37	10.1, 9.4	
	55	12.4	11.2±0.7; mean for 300° = 11.0±0.5

However, ΔH for the process, colloid = *F*-centers, can readily be evaluated from the slope of the curve of Fig. 4, in which the logarithm of the equilibrium concentra-

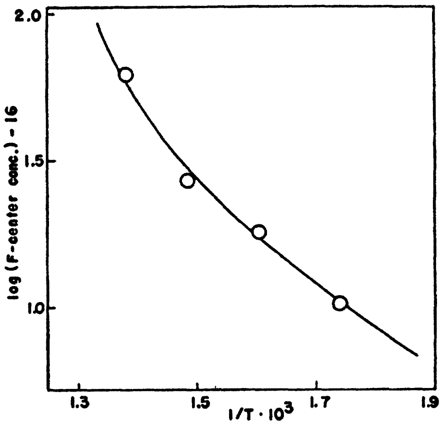

FIG. 4. Variation of the saturation concentration of *F*-centers with temperature.

tion is plotted against $1/T$; and it is found to be 8.0±0.3 kcal/mole of F-centers formed at 350° and is reasonably constant over the range 300°–400°. From Fig. 4 it may also be seen that a concentration of F-centers in the neighborhood of 7.0×10^{17}/cc would be stable at 500°, while at 250° the stable concentration would be about 3×10^{16}. Further extrapolation in either direction would yield stability values of qualitative value only. Errors due to changes during quenching may be expected to play an increasing part at temperatures above 400°; and, even if analytical means for the denser crystals were available, it would be necessary to make the absorption measurements at the equilibrium temperature, where broadening of the bands would cause serious interference.

Whether or not the coagulated centers are considered colloidal depends on the definition of the term "colloidal." Since a phase change occurs during the coagulation, the term appears appropriate, though light-scattering experiments have not as yet demonstrated the presence of colloidal material as was accomplished in the case of NaCl. E. Burstein and J. J. Oberly[9] have observed only slight photoconductance for KBr containing the R'-band, when illuminated with light of wavelength lying within the band, which is to be expected if the centers are mainly colloidal. It would be interesting to carry out the experiments on crystals in which the colloidal band has been developed in the absence of R- and N-bands.

(B) Shift of the Colloidal Band Maximum

The maximum absorption of the colloidal band was observed between 750 and 775 mμ, but a definite shift toward longer wavelength was observed at the higher treatment temperatures. This may be caused either by a change in the size distribution of the colloidal centers or by a thermal equilibrium between F- and M-centers, which have a maximum absorption at 825 mμ. A systematic study of the purely thermal relation between these two centers would add much to the understanding of the nature of M-centers.

No particular dependence of band shape or maximum other than an approximately symmetrical braodening and increase in height was observed with increasing concentration of the colloidal form. In the case of R'-bands observed[1] in very dense crystals (1×10^{19} color centers/cc) there was a broadening which included most of the spectrum from 600 to 1200 mμ and having a maximum absorption wavelength varying with thermal and optical treatment.

The colloidal band was virtually unaltered when measured at the temperature of liquid nitrogen.

(C) Additional Conclusions

R- and N-bands were never observed either accompanying the colloidal band nor following its reconversion to the F-band, which shows that these centers are not the initial steps in the thermal coagulation of F-centers.

The homogeneity of the $F-R'$ equilibrium previously described[1] is readily accounted for by the fact that both crystals studied were unsaturated with respect to F-centers at 450°, and therefore no second phase was present. Owing to the interference of the optically-produced centers, this was not discernible from the absorption curves alone, although with the present knowledge that the colloidal centers absorb strongly at 760 mμ it may be inferred from the general shape of the curves.

A reason, in addition to the possibilities already suggested,[2] for the extremely variable susceptibility change when F-centers were converted to R'-centers by 15 minutes' heating at 300°, is that equilibrium was not attained in that time. Complete conversion to a colloidal form should result in a loss of 98 percent of the paramagnetism of the F-centers; complete attainment of the saturation concentration of F-centers, in the absence of any small paramagnetic centers of the R- and M-type, should result in a loss of about 96 percent. The smaller change, on the average, may be accounted for on the basis of either incomplete conversion, the presence of other paramagnetic centers, or both. The acceleration of the conversion as indicated by the results with the faraday balance, by combined illumination and heat treatment, is at present under study in this laboratory. Unfortunately, the extension of magnetic investigations to the concentration range in which optical analytical means may be used would be a problem involving extreme experimental difficulties.

The interest and support of the Office of Naval Research, and the valuable assistance of Ray F. Palmer in conducting some of the pH experiments, is gratefully acknowledged.

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[9] E. Burstein (private communication).